Supporting Information:

Heterogenized Iridium Water-Oxidation Catalyst from a Silatrane Precursor

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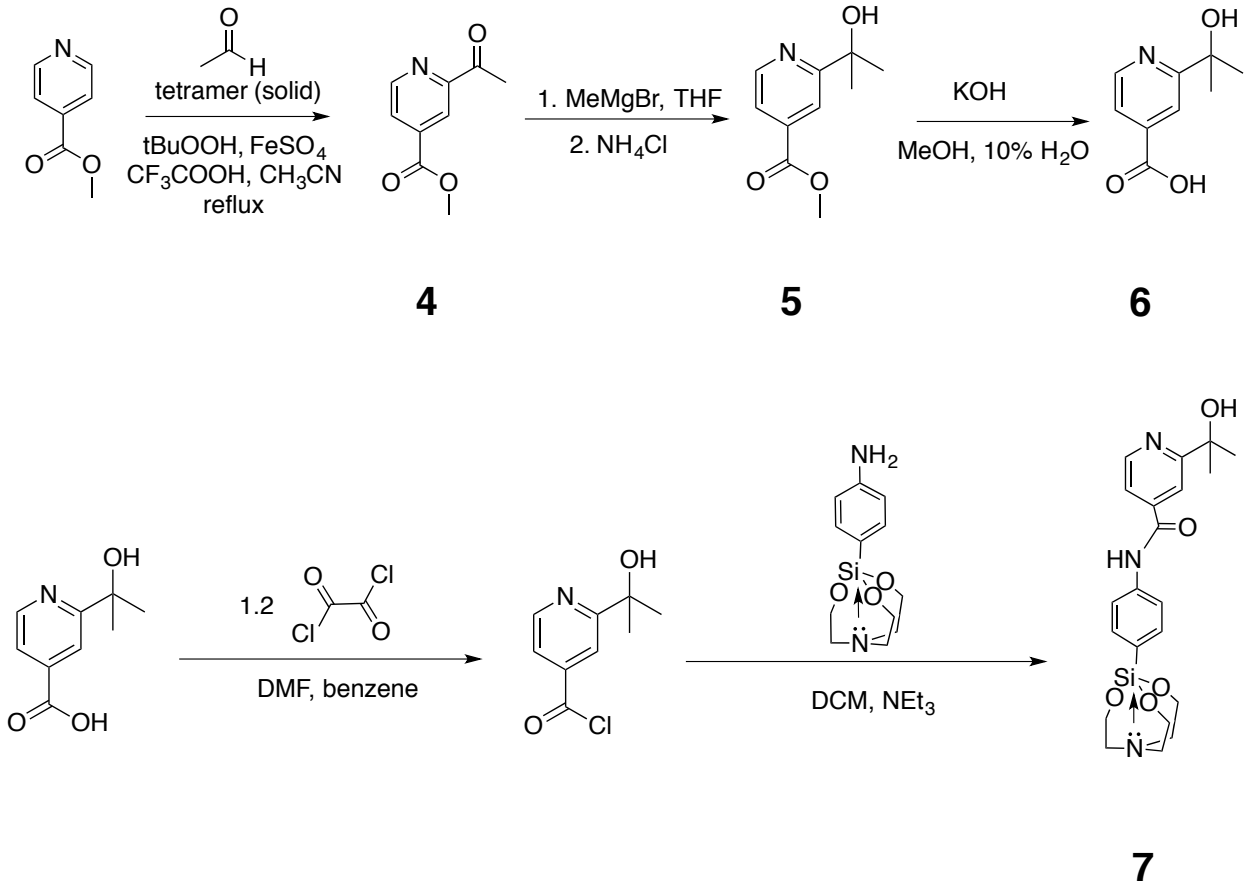
Experimental:

Materials: The chemicals used for the syntheses include: Methyl isonicotinate (98% Alfa Aesar), metaldehyde (Alfa Aesar), Iron (II) sulfate heptahydrate (99+% ACS, Strem), trifluoroacetic acid (99.5% Alfa Aesar), tert-Butyl hydroperoxide (70% aq. Solution, Alfa Aesar), methyl magnesium bromide (3M in ether, Alfa Aesar), and *p*-tolyltrimethoxysilane (Gelest). The remaining solvents and reagents used were purchased from commercial vendors.

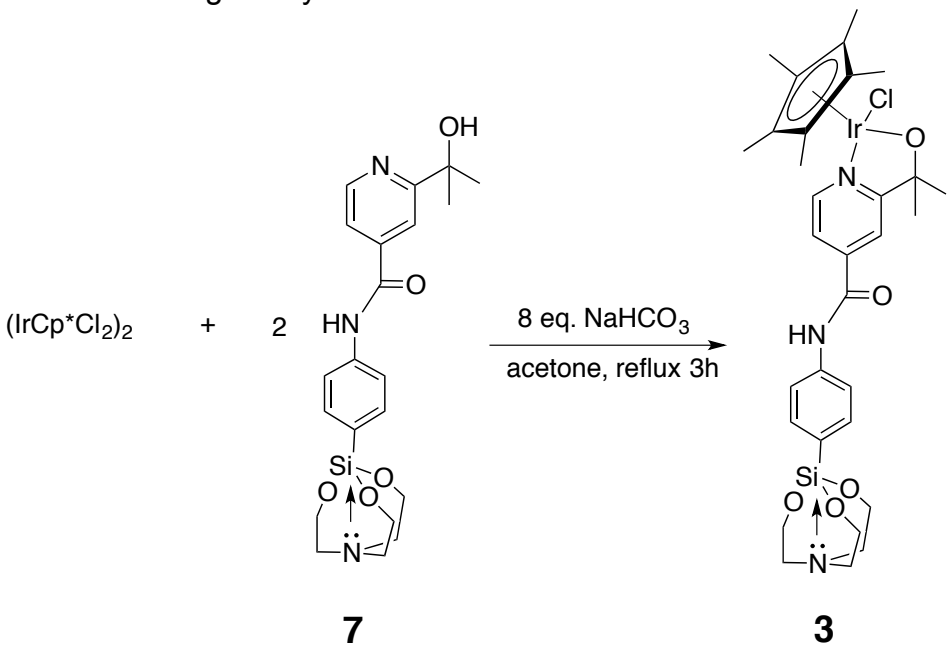
Instruments: A Varian 400 MHz instrument was used for the nuclear magnetic resonance measurements with values corresponding to ppm versus an internal TMS reference; J values are given in Hz. Mass spectrometry analysis was performed using an Agilent Technologies single quadrupole LCMS (LC-1250 Infinity liquid chromatogram/ 6120 single quadrupole mass spectrometer) with an Eclipse Plus C18 column (3.5 μM). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic measurements were performed using an Agilent Technologies Cary 600 series FTIR spectrometer and a PIKE technologies GladiATR. A Shimadzu UV-2600 spectrophotometer was used for UV-visible spectra acquisition. A Hitachi SU-70 analytical scanning microscope was used for SEM-EDX measurements. A Clark-type polarographic electrode was used for O_2 measurements.

Electrochemical measurements were performed using a Pine Wavenow potentiostat or a Princeton Applied Research VersaSTAT4 potentiostat. During cyclic voltammetry or electrolysis, a Ag/AgCl (saturated NaCl) reference electrode, manufactured by BASi, and a Pt wire auxillary electrode were used. To convert measured potentials to NHE, 0.206 V (calculated by BASi) was added to the Ag/AgCl (saturated NaCl) values.[1]

O_2 measurements were performed in an air-tight electrochemical cell containing **3**-*nano*ITO as the working electrode, a Ag/AgCl (saturated with NaCl) reference electrode, Pt counter electrode, a Clark-type electrode for O_2 detection, and a 0.1 M KNO_3 (pH 5.8) electrolyte. The air-saturated O_2 concentration in water was calculated prior to catalytic measurements and was used to calculate baseline readings.[2] During the electrochemical O_2 assays, no applied bias was taken during the first ten minutes of each experiment to get a baseline reading. After the baseline reading, a bias of 1.35 V vs. NHE was applied to the electrochemical cell to initiate water-oxidation catalysis.



Scheme S1: Ligand synthetic route.

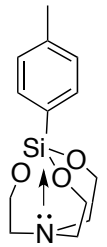


Scheme S2: Metal complex synthetic route.

Syntheses:

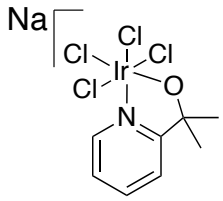
Pentamethylcyclopentadienyl iridium dichloride dimer, $(IrCp^*Cl_2)_2$,[3] 3-aminophenylsilatrane,[4] and Cp*Ir(2-(2'-pyridyl)-2-propanolate)Cl (Cp* = pentamethylcyclopentadienyl),[5] were synthesized and characterized by previously reported methods.

p-tolyl silatrane:



4.516 g triethanolamine (30 mmol) and 6.421 g *p*-tolyltrimethoxysilane were placed in a dry round bottomed flask. The reaction was heated under a nitrogen atmosphere in a closed system at 90 °C causing a white precipitate and refluxing of the methanol product. After three hours, the methanol was removed by distillation from the reaction. Once the majority of the methanol was removed, the reaction was cooled, filtered, and washed with cold methanol to yield *p*-tolylsilatrane as a white solid (7.588 g, 29 mmol, 95%).
(*p*-tolyl silatrane): ^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 400 MHz): δ 7.65 – 7.57 (2H, m, CH), 7.12 – 7.04 (2H, m, CH), 3.89 (6H, t, *J* = 5.9 Hz, CH_2), 2.90 (6H, t, *J* = 5.9 Hz, CH_2), 2.27 (3H, d, *J* = 0.6 Hz, CH_3).

$Na[Cl_4Ir(2-(2'-pyridyl)-2-propanolate)]$:

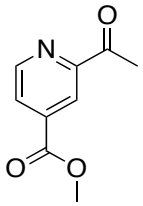


To 100 mL of saturated aqueous NaCl solution was added 700 mg (2.0 mmol) $IrCl_3 \cdot 3H_2O$ and 274 mg (2.0 mmol) 2-(2'-pyridyl)-2-propanolate). The solution was heated for 24 hours at 95 °C then washed twice with approximately 30 mL dichloromethane. The aqueous portion was oxidized with excess sodium periodate and evaporated under reduced pressure to a slurry. This was extracted three times with approximately 20 mL portions of dichloromethane. The extract was concentrated under reduced pressure and then partially purified by loading onto a short silica gel plug and flushing with acetone until only orange color remained on the silica. The solution was once again evaporated, loaded on a silica gel column, and eluted with ethyl acetate. The product was collected as a dark green band, evaporated to dryness, and washed

carefully with dichloromethane to give a nearly black powder. Yield: 80.4 mg, 7.5 %. For NMR characterization, an aliquot of the product was reduced to the diamagnetic Ir(III) state by briefly refluxing in isopropanol until the solution turned light yellow, then evaporating to dryness.

(Na[Cl_4Ir(2-(2'-pyridyl)-2-propanolate)]): ^{1}H NMR (D_2O, 600 MHz, Ir^{III} reduced state): δ 9.26 (1H, d , $^3J_{HH}$ = 6.1 Hz, CH), 7.94 (1H, t, $^3J_{HH}$ = 7.9 Hz, CH), 7.52 (1H, t, $^3J_{HH}$ = 6.7 Hz, CH), 7.46 (1H, d, $^3J_{HH}$ = 8.1 Hz, CH), 1.79 (6H, s, CH_3). ^{13}C {^{1}H} NMR (D_2O,150 MHz,): δ 171.0, 150.6, 139.8, 125.7, 123.2 (py), 88.9 (quat. C), 32.3 (Me). HRMS (FT-ICR, Ir^{IV} oxidized state): m/z calculated for $[C_8H_{10}NOIrCl_4]^-$ [M^-]: 468.91175 (z = 1-) Found: m/z = 468.91110 (z = 1-).

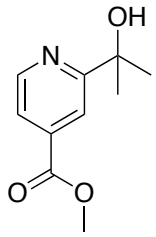
4:



The synthesis of **4** was based off of a previously reported method.[6] Methyl isonicotinate (3.29 mL, 27.8 mmol), metaldehyde (24.58 g, 139 mmol), and acetonitrile (90 mL) were combined and added to a round-bottomed flask, which formed a white cloudy mixture. The mixture was stirred at room temperature in air for ten minutes. To the mixture, iron(II) sulfate heptahydrate (0.124 g, 0.446 mmol), trifluoroacetic acid (3.24 g, 28.4 mmol), and 70% *tert*-butyl hydroperoxide (6.97 g, 77 mmol) was added, which formed a cloudy light pink mixture. The mixture was put under a nitrogen atmosphere and heated to reflux for 3.5 hours. During that time, the mixture changed from white cloudy to orange cloudy after ten minutes of reflux; after an hour of reflux, the solution became orange clear and finally became a deep red-brown clear solution. The solution was cooled to room temperature and the solvent removed by rotary evaporation, which provided a brown-red solid. The solid was taken up in 50 mL of $NaHCO_3$ (aq) and was extracted with toluene (3 x 40 mL). The toluene layer was dried over $MgSO_4$, filtered, and solvent removed via rotary evaporation. A brown liquid was obtained. The product (2.332 g, 13 mmol, 46%) was purified via silica gel chromatography using 1:4 ethyl acetate to hexane as the eluent.

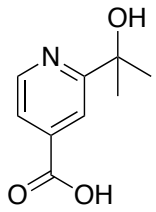
(4): ^{1}H NMR ($CDCl_3$ with 0.05% v/v TMS, 400 MHz,): δ 8.85 (1H, d, *J* = 5.0 Hz, CH), 8.53 (1H, d, *J* = 2.1 Hz, CH), 8.03 (1H, dd, *J* = 5.0, 1.8 Hz, CH), 4.00 (3H, s, CH_3), 2.75 (3H, s, CH_3). ESI-MS (m/z): calculated for $C_9H_9NO_3$: 179; found 180, $[M+H]^+$.

5:



To a dry Schlenk flask under a nitrogen atmosphere, **4** (3.65 g, 20.3 mmol) was added. Dry THF (50 mL) was added to the flask, which formed a clear yellow solution upon stirring. The solution was stirred at 0 ^{o}C for 30 minutes. Then, methyl magnesium bromide (7.4 mL, 22 mmol) solution in 3.0 M diethyl ether was slowly added to the solution, which caused a red cloudy mixture to form. The red-orange cloudy mixture was stirred at 0 ^{o}C for 2.5 hours, warmed to room temperature, and stirred for thirty minutes. Saturated ammonium chloride (25 mL) was added to the mixture and stirred at room temperature for thirty minutes. The solvent was removed by rotary evaporation, resulting in a dark red brown solid. The solid was dissolved in a 1:1 mixture of saturated ammonium chloride (400 mL) and ethyl acetate (400 mL) and put into a separatory funnel. The ethyl acetate layer was extracted and rinsed with brine (2 x 250 mL). The ethyl acetate layer was dried over magnesium sulfate, filtered, and the solvent removed by rotary evaporation. The product was purified by silica gel chromatography by eluting with 2% acetone in dichloromethane to remove initial impurities and then slowly increasing the acetone concentration to 5% acetone in dichloromethane to obtain the product (1.361 g, 7 mmol, 45%).
(5): ^{1}H NMR (acetone-d6, 400 MHz): δ 8.71 (1H, dd, *J* = 5.0, 0.9 Hz, CH), 8.22 (1H, m, CH), 7.71 (1H, dd, *J* = 5.0, 1.6 Hz, CH), 4.74 (1H, s, OH), 3.95 (3H, d, *J* = 2.3 Hz, CH_3), 1.58 (6H, s, CH_3). ESI-MS (m/z): calculated for $C_{10}H_{13}NO_3$: 195; found: 196 $[M+H]^+$.

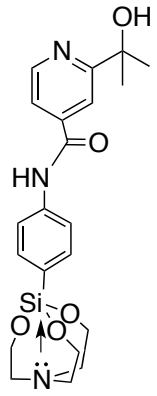
6:



To a round bottomed flask, **5** (0.0521 g, 0.26 mmol) and methanol (5 mL) were added. Potassium hydroxide (0.107 g, 1.9 mmol) was dissolved in 0.695 mL water and added to the round bottomed flask. The clear yellow solution was stirred at 40 ^{o}C for two hours. The solvent was rotary evaporated off, which provided an orange oil. The crude product was dissolved in ethyl acetate and brine, put into a separatory funnel, and the ethyl acetate layer collected. The brine layer was washed with ethyl acetate until the product was no longer visible in the water layer by TLC. The ethyl acetate layers were

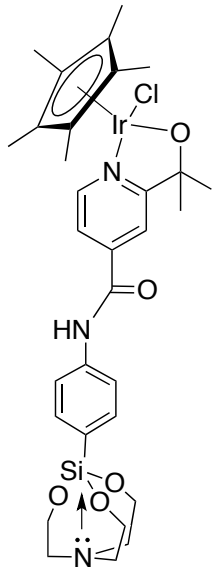
combined, dried over magnesium sulfate, filtered, and the solvent removed via rotary evaporation, which provided a white solid (0.0355 g, 0.195 mmol, 73%).
(6): ^{1}H NMR (CD_3OD with 0.05% v/v TMS, 400 MHz): δ 8.50 (1H, dd, *J* = 5.0, 0.9 Hz, CH), 8.13 – 8.08 (1H, m, CH), 7.67 (1H, dd, *J* = 5.1, 1.5 Hz, CH), 1.56 (6H, s, CH_3). Compound does not show OH peak due to being a potassium salt. However, it becomes protonated in an LC-MS column. ESI-MS (m/z): calculated for $C_9H_{11}NO_3$: 181; found 182 $[M+H]^+$.

7:



To a dry Schlenk flask under a nitrogen atmosphere with a stir bar, **6** (0.168 g, 0.00092 mol) was added. Dry benzene (30 mL) was added forming a yellow mixture when stirred at room temperature. Oxalyl chloride (0.09 mL, 0.001 mol) was added to the mixture, which turned the color slightly pink. One drop of anhydrous dimethylformamide was then added, which resulted in solubilization of the cloudy mixture. The solution was stirred at room temperature for 1.5 hours. Then, two-thirds of the benzene was pumped off of the solution under vacuum. Dichloromethane (30 mL) was added to the mixture forming an orange, cloudy mixture. Triethylamine (0.130 mL, 0.00093 mol) was added to the mixture, which resulted in a clear yellow solution. Then, 3-aminosilatrane was added to the solution, resulting in a golden yellow mixture. The mixture was stirred at room temperature for one hour. The solvent was removed by rotary evaporation, which resulted in a brown-yellow solid. The pure product (0.268 g, 0.62 mmol, 67%) was obtained by silica gel chromatography by eluting with 30% acetone in dichloromethane.
(7): ^{1}H NMR ($(CD_3)_2CO$ with 0.05% v/v TMS, 400 MHz): δ 9.62 (1H, s, NH), 8.65 (1H, dd, *J* = 5.0, 0.9 Hz, CH), 8.15 (1H, dd, *J* = 1.6, 0.9 Hz, CH), 7.73 (1H, dd, *J* = 5.1, 1.7 Hz, CH), 7.68 – 7.55 (4H, m, CH), 4.63 (1H, s, OH), 3.79 (6H, t, *J* = 5.9 Hz, CH_2), 2.97 (6H, t, *J* = 5.9 Hz, CH_2), 1.54 (s, 6H, CH_3). FT-IR: 1650 cm^{-1} (C=O), 1583 cm^{-1} (C=C pyalc), 1509 cm^{-1} (N-H), 1452 cm^{-1} (CH_2 silatrane cage), 1172 cm^{-1} (C-O silatrane cage). UV-Vis: 275 nm, 227 nm. ESI-MS (m/z): calculated for $C_{21}H_{27}N_3O_5Si$: 429; found 430 $[M+H]^+$.

3:



To a round-bottomed flask **7** (0.058 g, 0.13 mmol), Pentamethylcyclopentadienyl iridium dichloride dimer (0.054 g, 0.067 mmol), and acetone (25 mL) were added and stirred. Then, sodium bicarbonate (0.044 g, 0.52 mmol) was added to the orange cloudy mixture. The orange mixture was refluxed under nitrogen for four hours. Over time, the solution's nature changed from a light, orange cloudy mixture to a deep, orange clear solution. The reaction was cooled to room temperature, the excess salts filtered off, and the solvent evaporated off. The orange solid was dissolved in dichloromethane and layered with octane and kept in the freezer for twelve days. The product (0.099 g, 0.12 mmol, 93%) precipitated out as a red solid from the layered system.
(3): ^{1}H NMR ($(CD_3)_2CO$ with 0.05% v/v TMS, 400 MHz): δ 9.74 (1H, s, NH), 8.79 (1H, d, *J* = 5.8 Hz, CH), 7.77 – 7.71 (2H, m, CH), 7.65 – 7.56 (4H, m, CH), 3.80 (6H, t, *J* = 5.9 Hz, CH_2), 2.99 (6H, t, *J* = 5.9 Hz, CH_2), 1.66 (15H, s, CH_3), 1.43 (6H, s, CH_3). FT-IR: 2960 cm^{-1} (C-H pyalc), 2916 cm^{-1} (C-H pyalc), 2856 cm^{-1} (C-H pyalc and Cp*), 1660 cm^{-1} (C=O), 1590 cm^{-1} (C=C pyalc), 1520 cm^{-1} (N-H), 1452 cm^{-1} (CH_2 silatrane cage), 1174 cm^{-1} (C-O silatrane cage). UV-Vis: 229 nm, 280-320 nm broad. HR ESI-MS (m/z): calculated for $C_{31}H_{41}ClIrN_3O_5Si$: 791; found 791, 756 $[M-Cl]^+$.

Theoretical:

Geometry Optimizations: The minimum energy geometries (as confirmed by normal mode analysis) of **3** (both with hydrogen bonding waters and without) and **3**-TiO_2 were determined using the exchange-correlation functional B3LYP[7] combined with the basis set 6-311G(d,p) basis set[8-10] for H, C, O, N, Si, and Cl, together with LANL2DZ[11-13] for low-spin Ir(III) and Ti(IV), as implemented in the Gaussian 09 and its default optimization criteria and integration grid.[14] This level of theory has been utilized successfully in the determination of IR spectra in hydroxamates in similar clusters.[15] The atoms in **3** were allowed to fully relax. The structure of **3**-TiO_2 was created by using the lowest energy binding mode and cluster from our previous work.[16] Initially, the geometry

of the silatrane anchor was relaxed using p-tolyl-silanetriol (tolyl-silatrane) under the conditions that only the passivating edge hydroxyls were frozen. Then the structure was used as an initial geometry for the anchor as part of **3**-TiO_2. That structure was relaxed between the amide linkage up to the Cp*.

Vibrational Spectra: Frequencies and intensities for both **3** and **3**-TiO_2 were generated by diagonalizing the full Hessian. In the case of **3**-TiO_2**,** artifacts in the calculated spectrum occurring from the use of frozen atoms were compensated for by subtracting away the IR spectrum for the same cluster, but without the adsorbed molecule. The spectra were generated for both **3** and **3**-TiO_2 by convolution with Lorentzians with full-widths at half-maximum of 10 cm^{-1} and 12 cm^{-1}, respectively. For both **3** and **3**-TiO_2, harmonic frequencies were scaled with a factor of 0.955.

UV-visible spectra and related data:

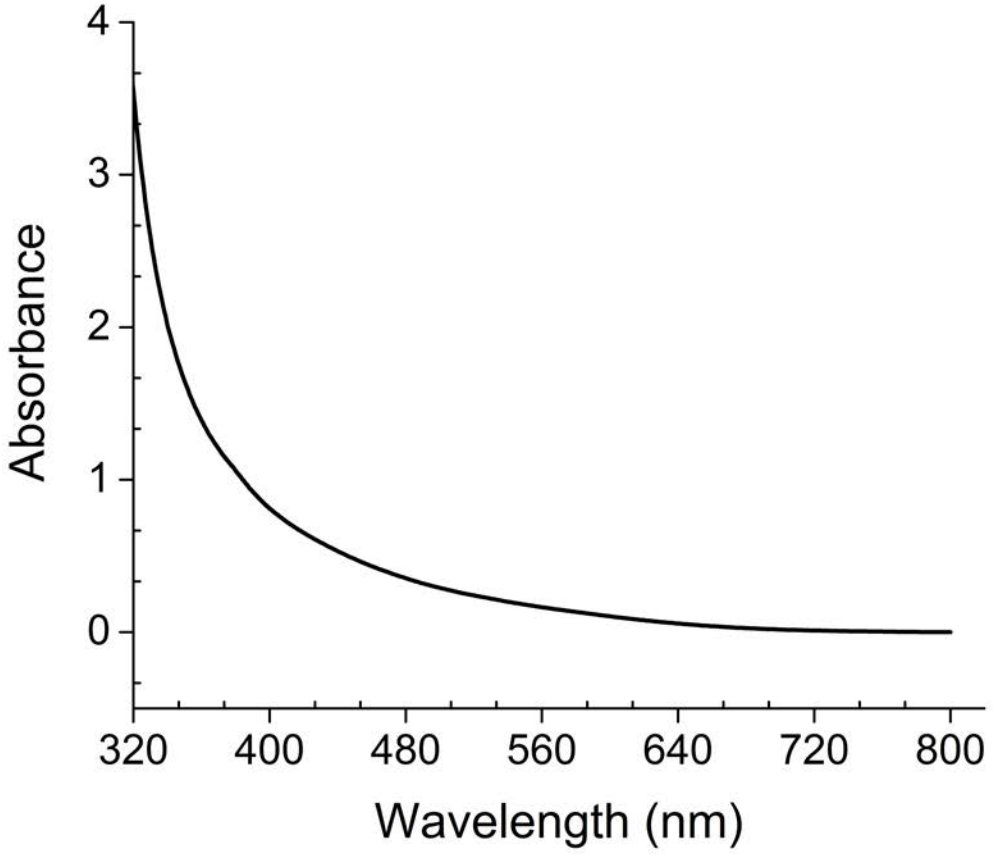


Figure S1. UV-visible spectrum of *nano*ITO on FTO coated glass substrate. Absorption of the glass occurs below 300 nm.

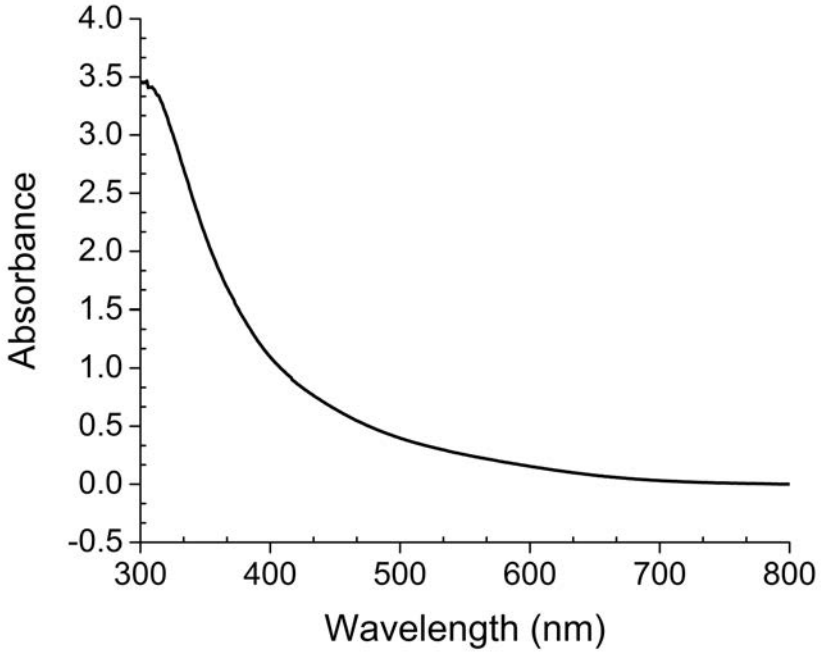


Figure S2. UV-visible spectrum of **3**-*nano*ITO. Absorption of the glass substrate occurs below 300 nm.

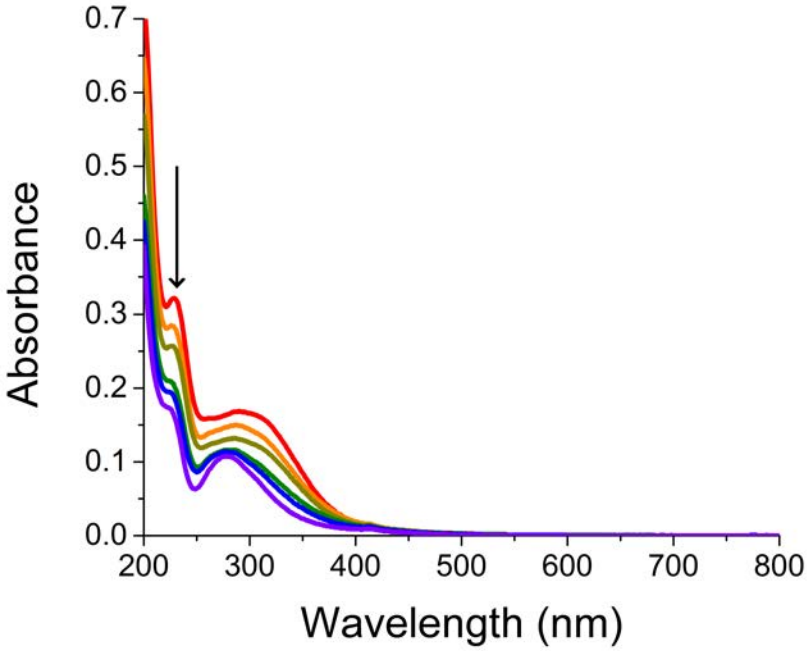


Figure S3. UV-visible spectra during sensitization of *nanoI*TO with complex **3**. The spectra are of complex **3** in acetonitrile taken over three hours as the electrodes are sensitized. The absorbance decreases over time (red to purple) indicating the complex is binding to the electrode surface.

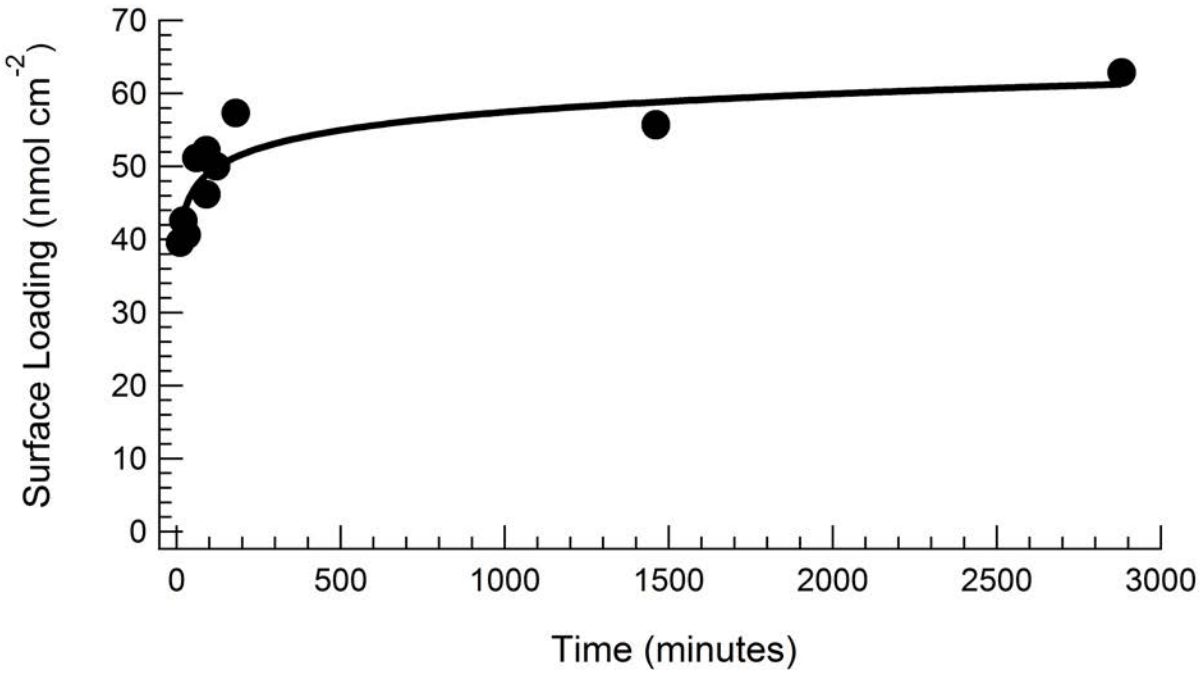


Figure S4. Surface loading plot of complex **3** on TiO_2 over 48 h of exposure. There is minimal loading change after 3 h of sensitization.

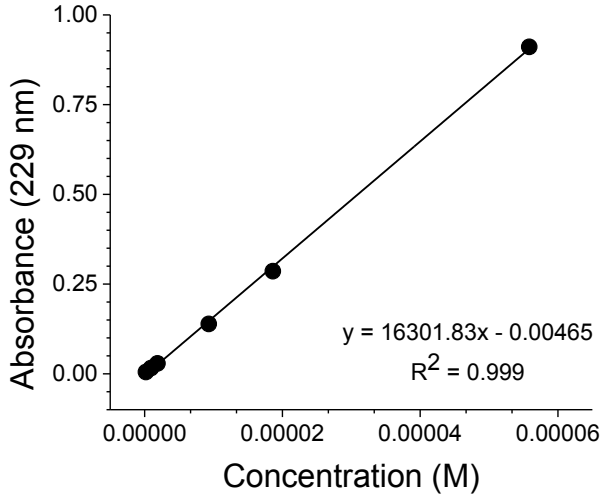


Figure S5. Beer's Law plot of complex **3** in acetonitrile. The molar absorptivity at 229 nm was found to be 16,301 M^{-1} cm^{-1}.

Energy Dispersive X-ray Analysis Data:

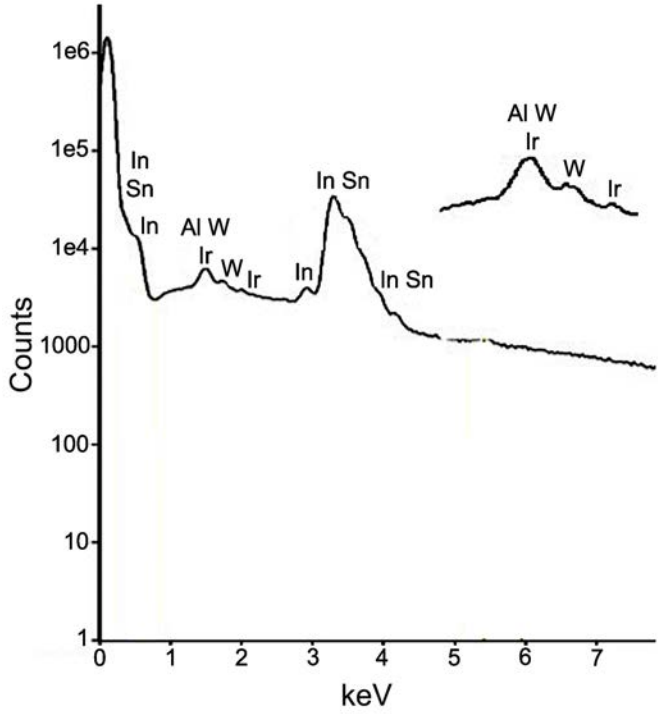


Figure S6. EDX spectrum of **3**-*nano*ITO. Al and W peaks are from the sample stage. The inset is an enlargement of the spectrum between 1-3 keV.

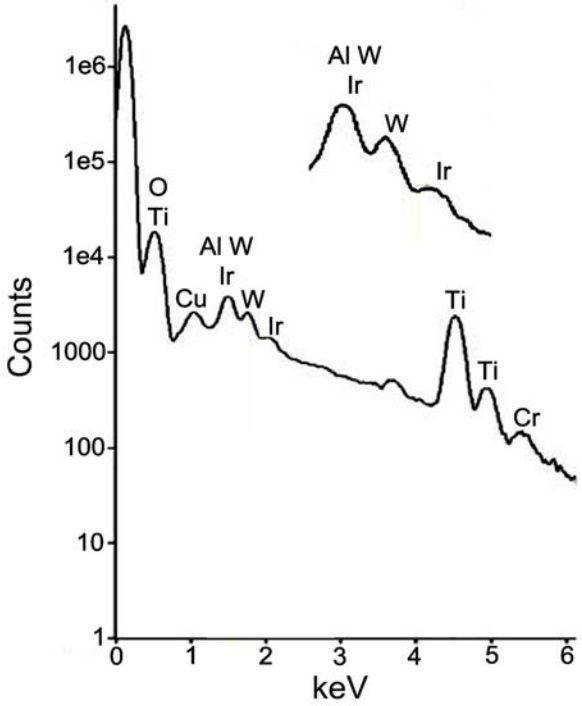


Figure S7. 3-TiO_2 EDX spectrum. Cu, Al, W, and Cr peaks are from the sample stage. The inset is an enlargement of the spectrum between 1.5-2.5 keV.

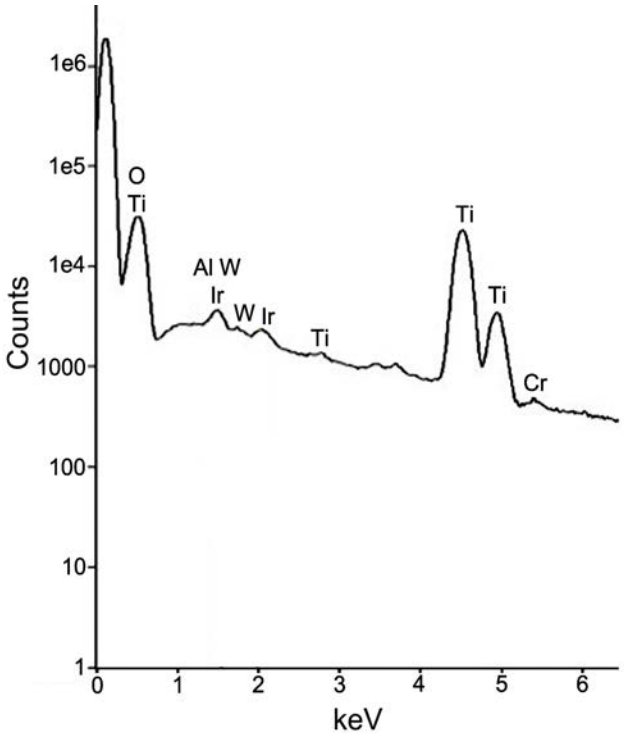


Figure S8. 3-TiO_2 post electrolysis at 1.35 V vs. NHE for 1 h EDX spectrum. Al, W, and Cr peaks are from the sample stage.

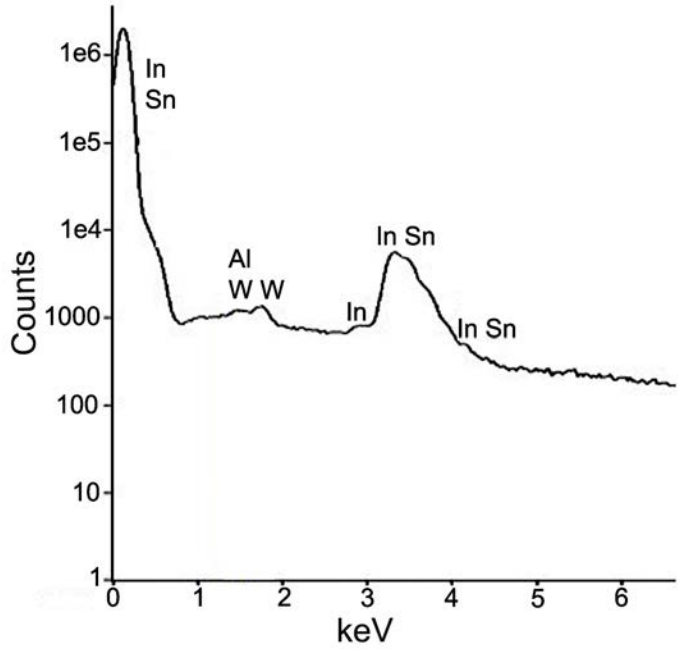


Figure S9. *nano*ITO blank electrode EDX spectrum. Al and W peaks are from the sample stage.

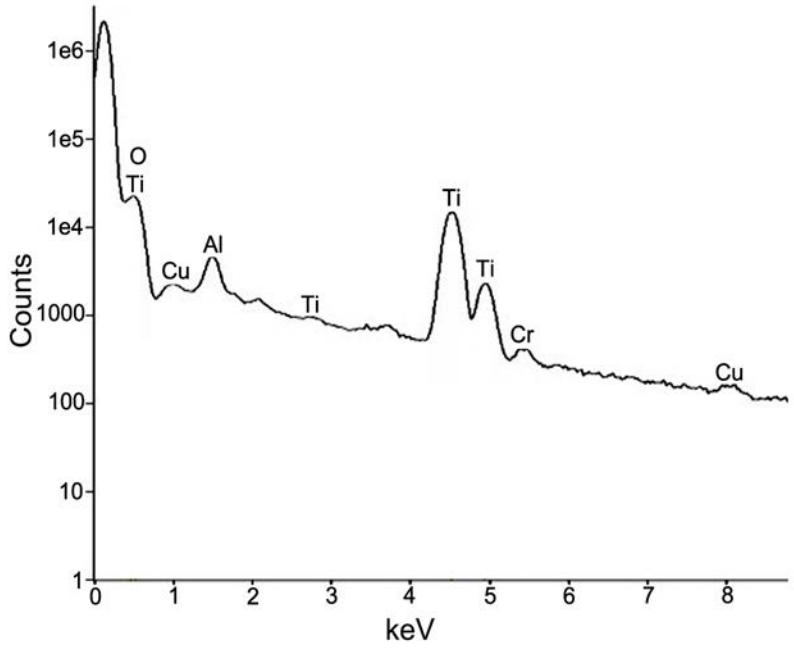


Figure S10. TiO_2 EDX spectrum. Cu, Al, and Cr peaks are from the sample stage.

Theoretical IR Spectra and Optimized Structures:

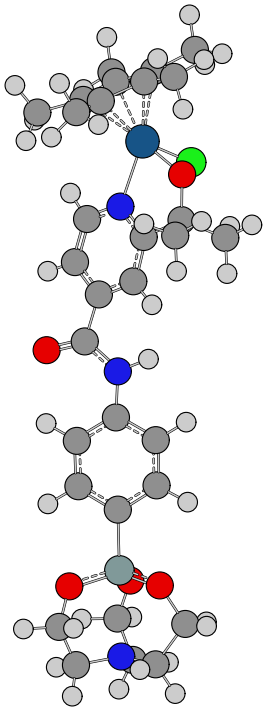


Chart S1. Calculated geometrically optimized structure of **3** without considering water hydrogen bonding. Atom labels: carbon (dark grey), hydrogen (light grey small sphere), oxygen (red), nitrogen (small blue sphere), iridium and (large blue sphere).

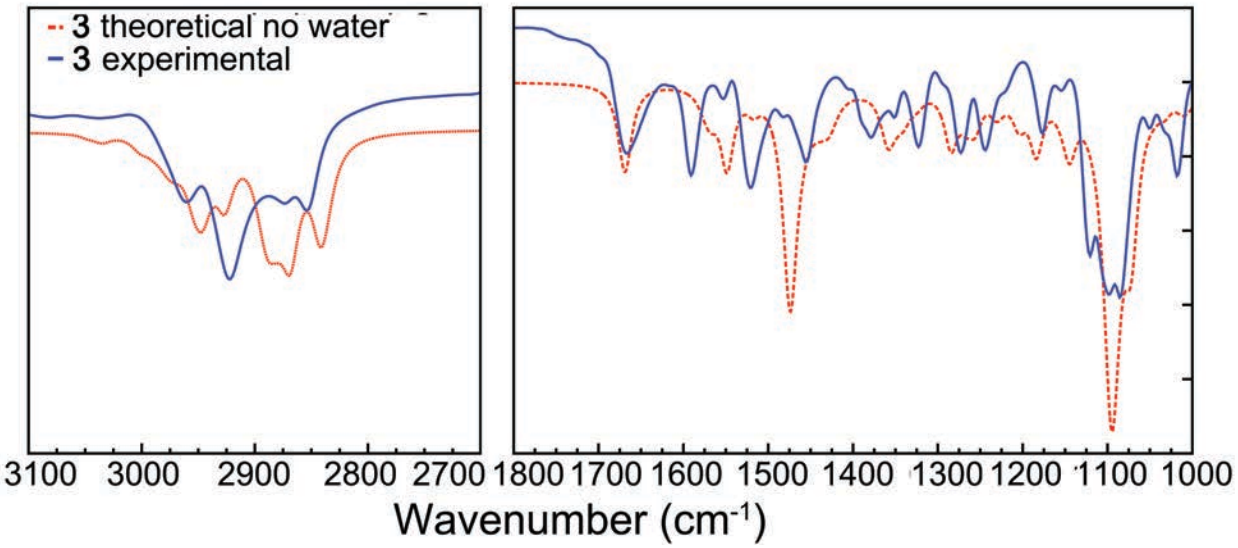


Figure S11. ATR-FTIR spectra of experimental **3** vs. calculated **3** (no hydrogen bonding to water considered).

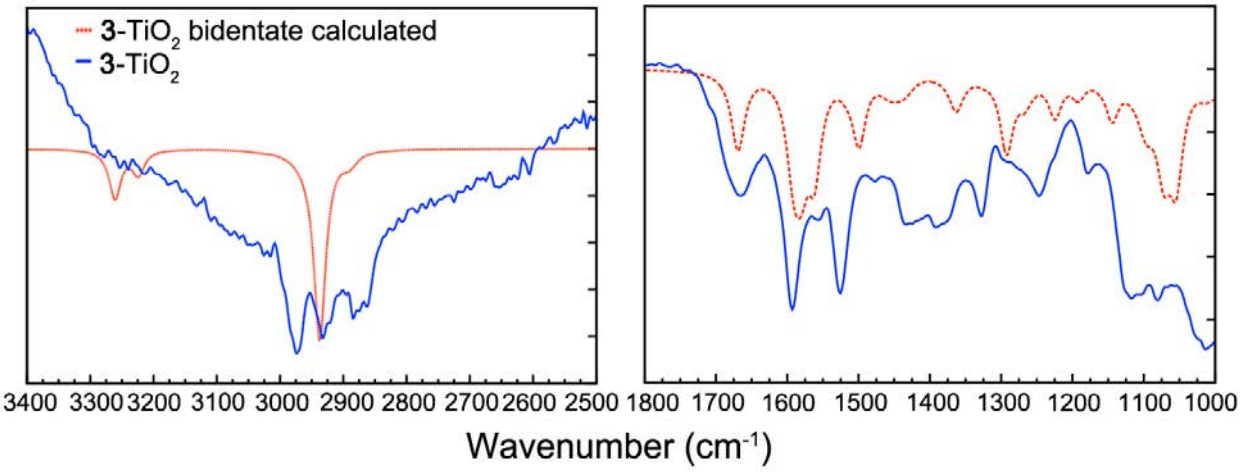


Figure S12: ATR-FTIR spectra of **3**-TiO_2 and simulated **3**-TiO_2 with a bidentate siloxane binding mode and hydrogen-bonding water molecules.

Table S1. Experimental and theoretical (scaled by 0.955) frequencies.

	C-O of cage	CH_2 of cage	N-H bend	C=C stretch	C=O stretch	alkoxide methyl C-H stretch	Cp* methyl C-H stretch
Expt.	1170	1452	1515	1590	1689	2856, 2916, and 2960	2856, 2960
Theor. **3** without waters	1095	1429	1474	1568	1669	2880, 2891, 2955	2879, 2888
Theor. **3** with waters	1096	1427	1503	1578	1664	2888, 2901, 2963	2880, 2889
Theor. **3**-TiO_2 with waters	-	-	1499	1578	1669	2888, 2899, 2963	2881, 2890

Experimental ATR-FTIR Spectra:

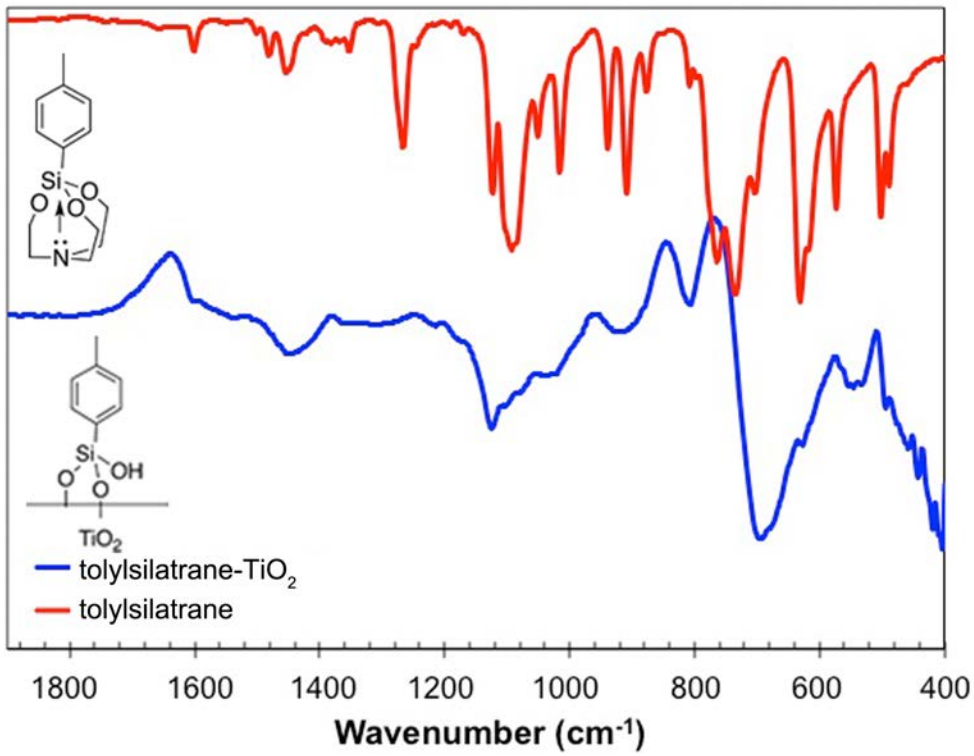


Figure S13. ATR-FTIR spectra of p-tolyl silatrane (red) vs. p-tolyl silatrane-TiO_2 (blue).

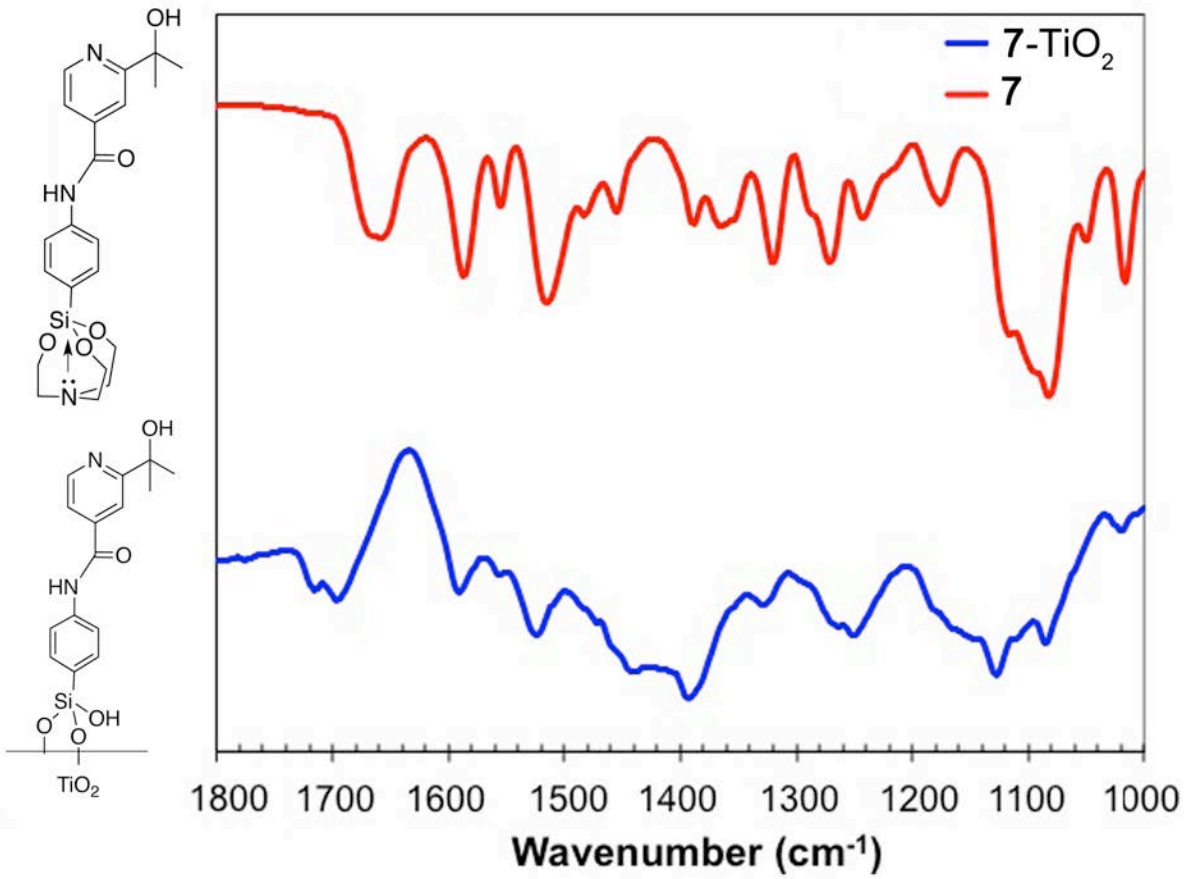


Figure S14. ATR-FTIR spectra of **7** (red) vs. **7**-TiO_2 (blue); TiO_2 background subtracted from **7**-TiO_2 spectrum.

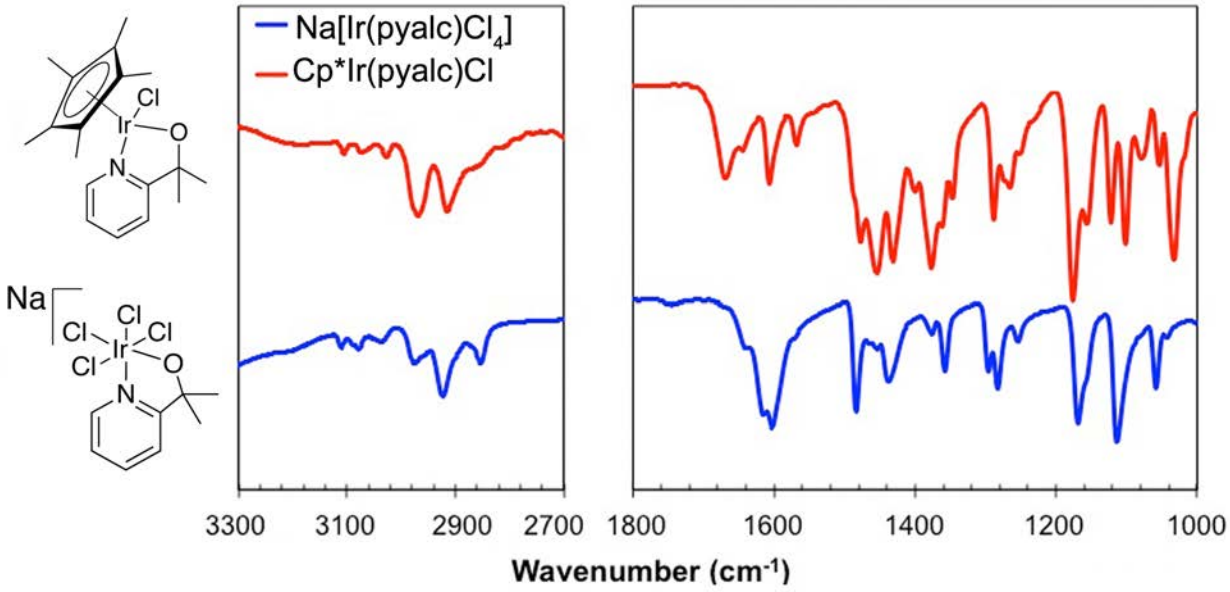


Figure S15. ATR-FTIR spectra of Na[Cl_4Ir(2-(2'-pyridyl)-2-propanolate)] (blue) vs. Cp*Ir(2-(2'-pyridyl)-2-propanolate)Cl (red); 2-(2'-pyridyl)-2-propanolate is abbreviated as pyalc.

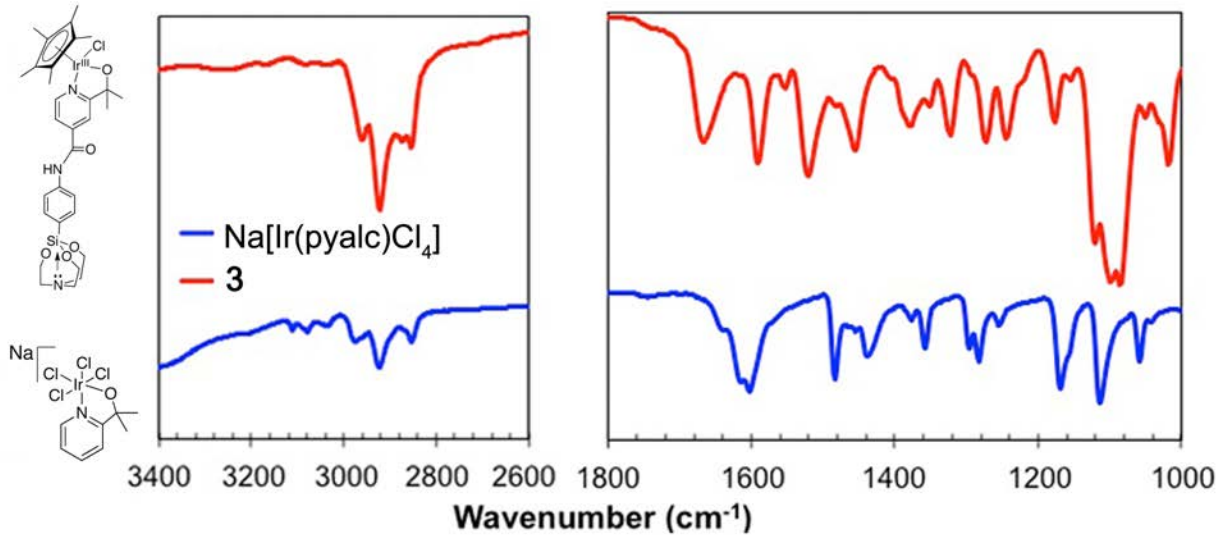


Figure S16. ATR-FTIR spectra of Na[Ir(2-(2'-pyridyl)-2-propanolate)Cl_4] (blue) vs. **3** (red). 2-(2'-pyridyl)-2-propanolate is abbreviated as pyalc.

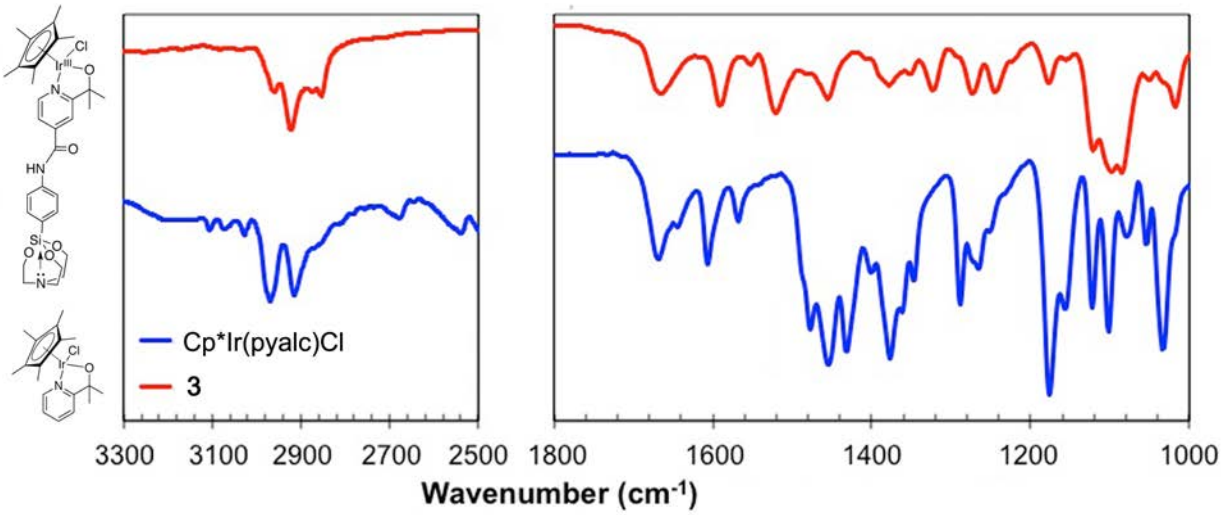


Figure S17. ATR-FTIR Cp*Ir(2-(2'-pyridyl)-2-propanolate)Cl (blue) vs. **3** (red). 2-(2'-pyridyl)-2-propanolate is abbreviated as pyalc.

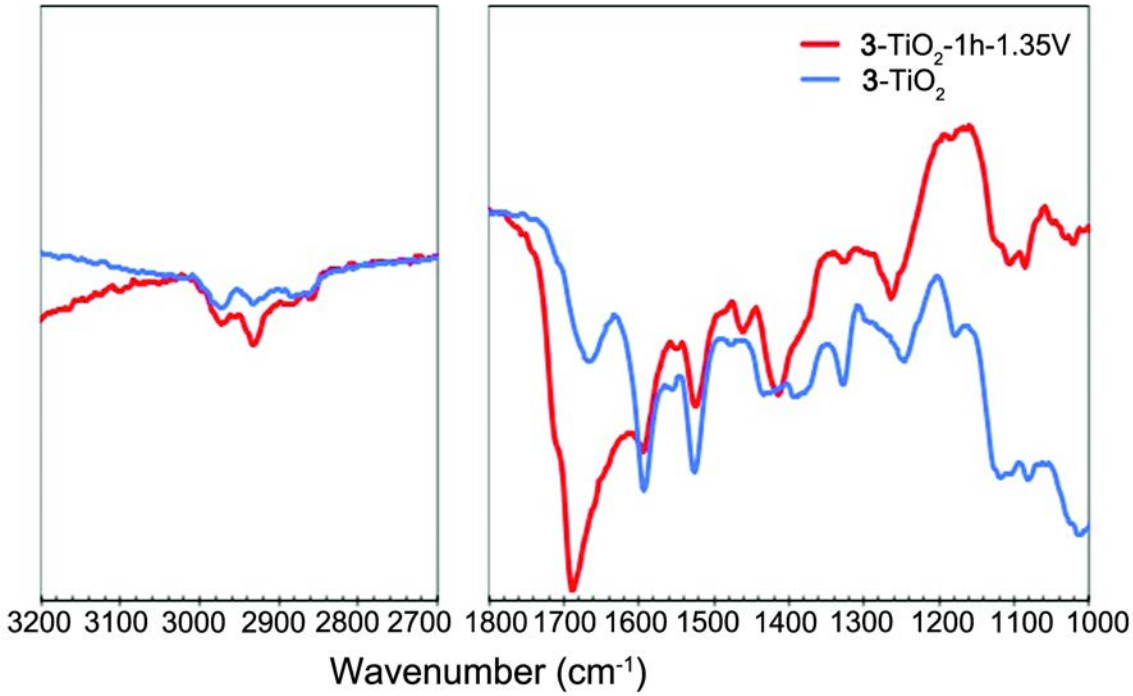


Figure S18. ATR-FTIR spectra of **3**-TiO_2 (blue) and **3**-TiO_2 (red) post 1 h electrolysis at 1.35 V vs. NHE.

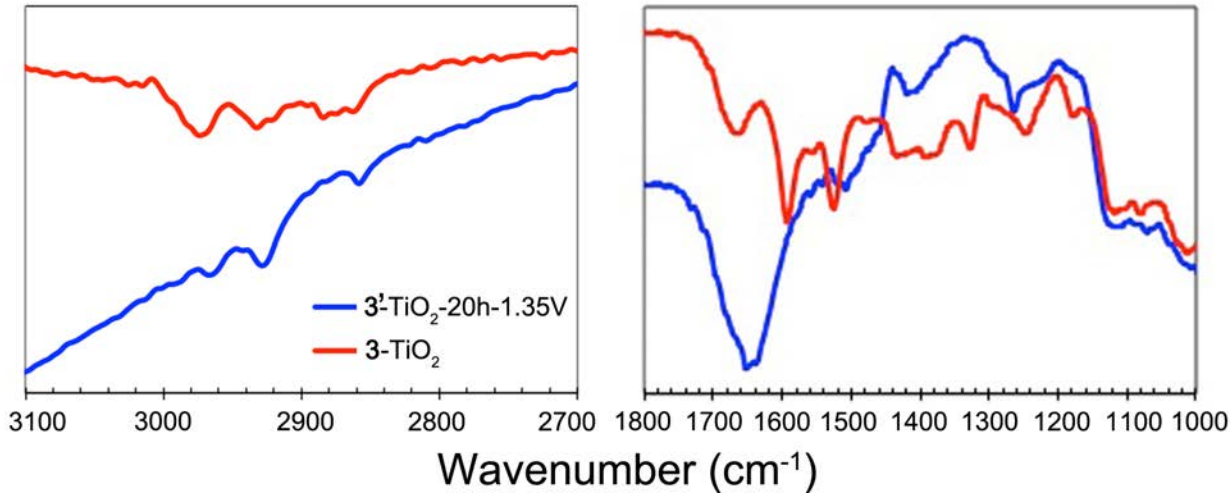


Figure S19. ATR-FTIR spectra of **3**-TiO_2 (red) and **3'**-TiO_2 post 20 h electrolysis at 1.35 V vs. NHE (blue).

Electrochemical Data:

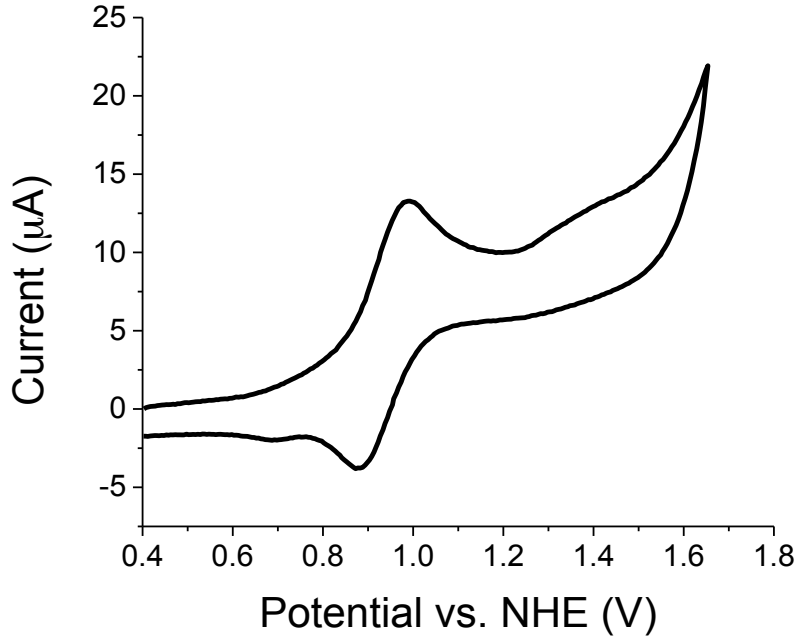


Figure S20. Cyclic voltammogram of **3** in 0.1 M $TBAPF_6$/acetonitrile using a Pt working electrode. An iridium (III/IV) redox couple is observed at 0.93 V vs. NHE and an iridium(IV/V) redox couple appears at 1.35 V vs. NHE. A scan rate of 50 mV/s was used.

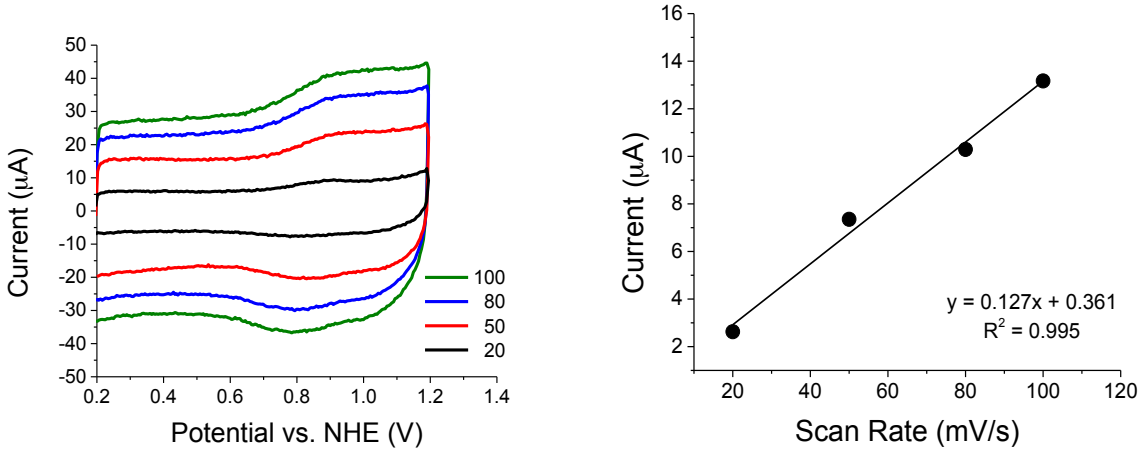


Figure S21. Left: Scan rate dependence cyclic voltammograms of **3**-*nano*ITO at 100 (green), 80 (blue), 50 (red), and 20 mV/s (black); Right: Capacitance-subtracted current vs. scan rate plot for **3**-*nano*ITO.

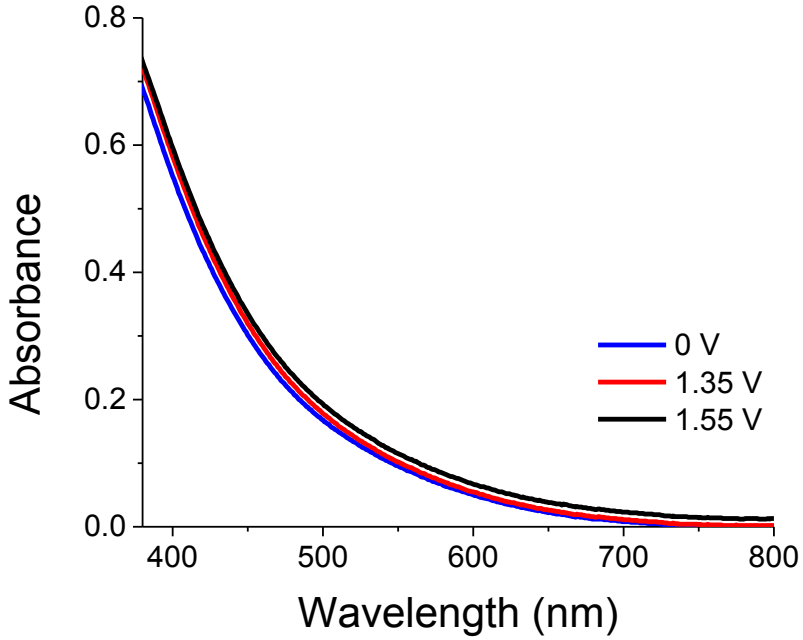


Figure S22. Spectroelectrochemical experiments showing the *nano*ITO background-subtracted UV-visible spectra during an applied bias of 0 V (blue), 1.35 V (red), and 1.55 V (black) vs. NHE to **3**-*nano*ITO.

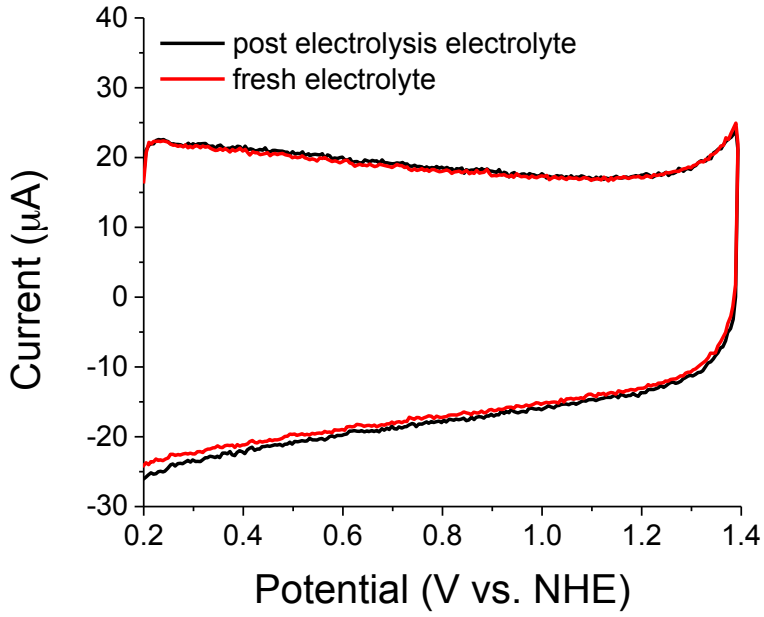


Figure S23: CVs of *nano*ITO blank electrodes in fresh 0.1 M KNO_3 compared to used 0.1 M KNO_3 after a 20 hour electrolysis of *nano*ITO-**3** at 1.35 V vs. NHE.

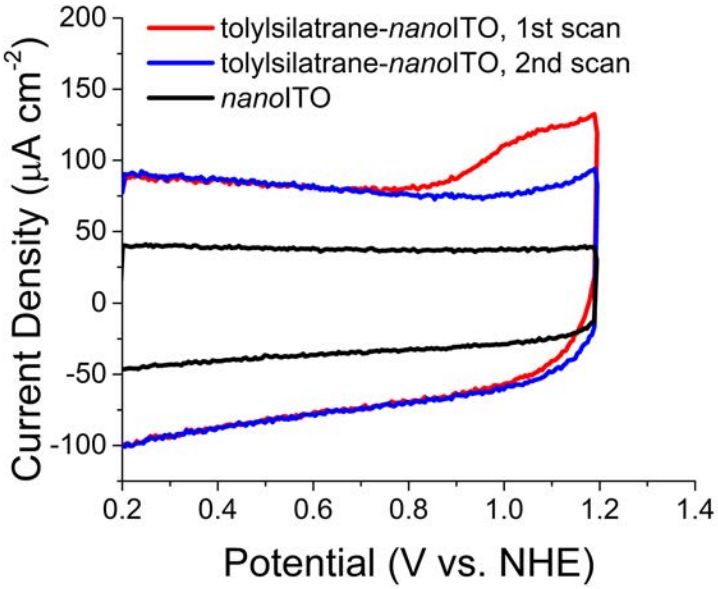


Figure S24. CV traces of tolylsilatrane-*nano*ITO electrodes in 0.1 M KNO_3. The red trace is the first CV taken of tolylsilatrane-*nano*ITO and the blue trace is the second CV trace of the same electrode. A blank *nano*ITO electrode CV trace is shown in black.

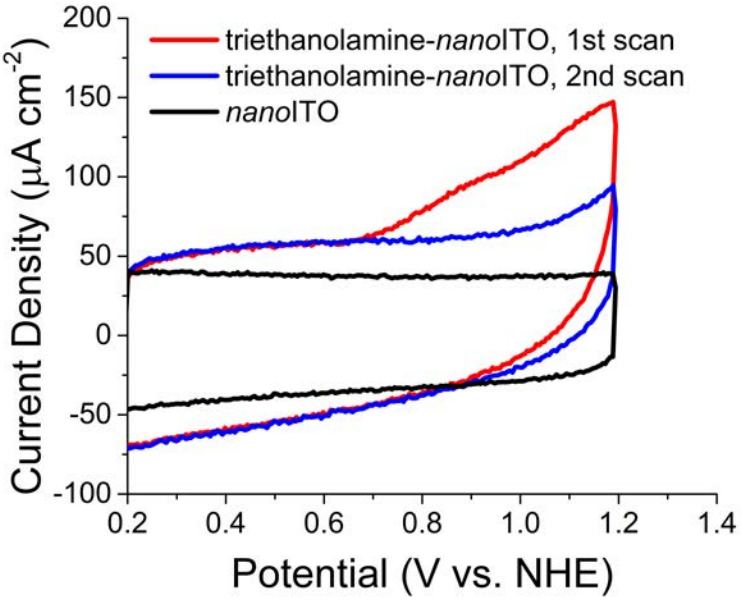


Figure S25. CV traces of triethanolamine-*nano*ITO electrodes in 0.1 M KNO_3. The red trace is the first CV taken of triethanolamine-*nano*ITO and the blue trace is the second CV trace of the same electrode. A blank *nano*ITO electrode CV trace is shown in black.

Oxygen Evolution:

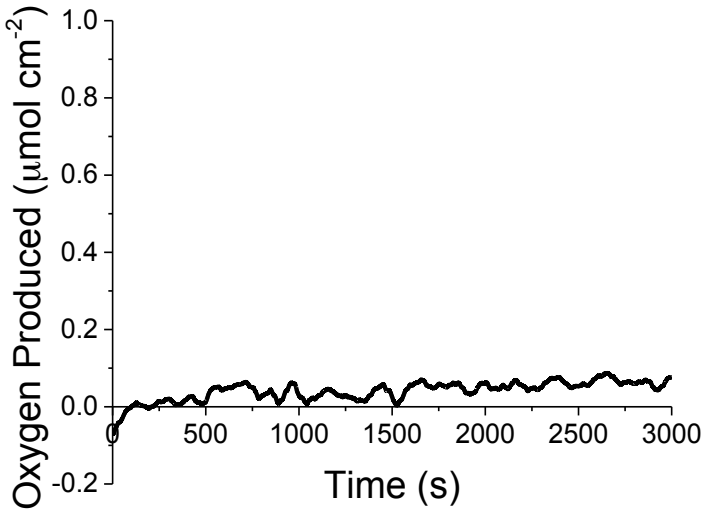


Figure S26. Oxygen assay of *nano*ITO blank working electrode in 0.1 M potassium nitrate. A potential of 1.35 V vs. NHE was applied at 600 s.

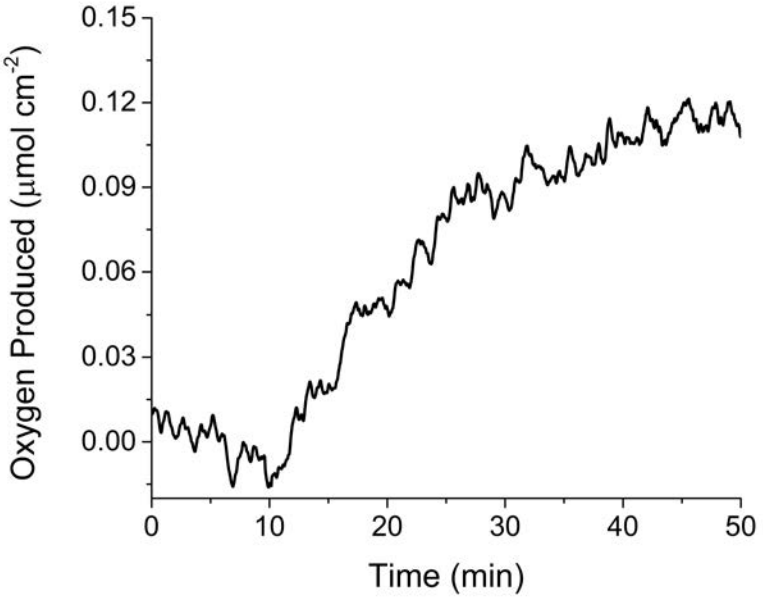


Figure S27. Oxygen assay of **3**-*nano*ITO working electrode in 0.1 M sodium triflate. A potential of 1.45 V vs. NHE was applied at 10 minutes.

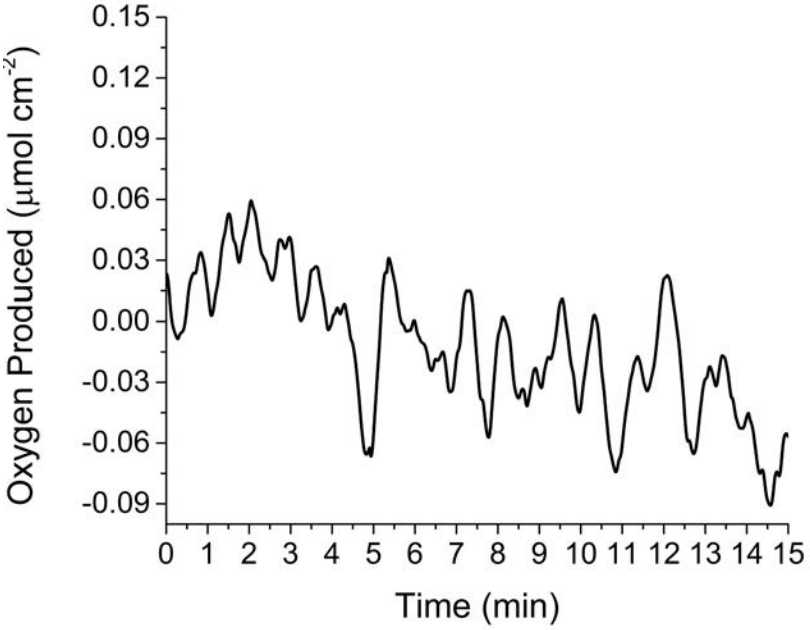


Figure S28. Oxygen assay of *nano*ITO blank working electrode in 0.1 M sodium triflate. A potential of 1.45 V vs. NHE was applied from 5-10 minutes.

Theoretical Coordinates:

These coordinates are given as xyz files with a short descriptor and SCF energy in Hartrees the title line below:

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Complex **3** without water molecules. SCF Energy: -2601.48661225.

Ir	-5.03850	0.10980	-0.14510
C	-6.30710	-0.58490	1.47440
C	-6.95560	0.53980	0.83030
C	-6.21590	-1.65120	0.48370
C	-7.18840	0.20400	-0.54200
C	-6.74570	-1.17390	-0.75340
C	-5.74150	-3.04200	0.77070
H	-4.90880	-3.04740	1.47630
H	-6.55320	-3.62850	1.21540
H	-5.42430	-3.55890	-0.13620
C	-6.91840	-1.93620	-2.02920
H	-6.32630	-2.85240	-2.03450
H	-7.96880	-2.21600	-2.16940
H	-6.60410	-1.33560	-2.88440
C	-7.84830	1.05450	-1.58180
H	-7.33950	0.95340	-2.54120
H	-8.89620	0.75930	-1.70800
H	-7.82070	2.10940	-1.30930
C	-7.22590	1.85310	1.49670
H	-7.77240	2.52900	0.83960
H	-7.82020	1.70640	2.40330
H	-6.27980	2.33240	1.76460
C	-6.02490	-0.69980	2.94090
H	-5.73460	0.26510	3.35910
H	-6.91260	-1.04820	3.48260
H	-5.21670	-1.40510	3.14260
Cl	-4.32330	0.68360	-2.46370
C	-2.16080	0.55590	0.40190
C	-2.52290	-1.66710	-0.19840
C	-0.78850	0.31020	0.48290
C	-1.17980	-1.97040	-0.11820
H	-3.25160	-2.40730	-0.49610
C	-0.27860	-0.95640	0.21650
H	-0.13930	1.12180	0.78650
H	-0.82010	-2.97070	-0.31690
N	-3.00700	-0.43760	0.06530
C	-2.79040	1.92440	0.65440
O	-4.18240	1.83940	0.58090
C	-2.42030	2.41150	2.07420

H	-1.34540	2.57240	2.20330
H	-2.93300	3.35910	2.25100
H	-2.76170	1.69180	2.82190
C	-2.26720	2.92430	-0.40630
H	-2.74400	3.88950	-0.22260
H	-1.18100	3.05910	-0.35590
H	-2.54770	2.58410	-1.40300
C	1.18480	-1.31770	0.30980
O	1.52360	-2.45450	0.58970
N	2.04320	-0.28230	0.04570
H	1.61990	0.56680	-0.29730
C	3.45640	-0.27310	0.05290
C	4.08720	0.91180	-0.34880
C	4.23520	-1.36530	0.45090
C	5.47160	1.00090	-0.36210
H	3.48740	1.76650	-0.64940
C	5.62280	-1.25360	0.43050
H	3.75510	-2.27940	0.76340
C	6.27610	-0.08250	0.02190
H	5.93400	1.93380	-0.66390
H	6.21160	-2.10480	0.75370
Si	8.13770	0.02510	-0.04930
O	8.55180	-0.34050	-1.62500
O	8.46330	1.60910	0.36620
O	8.65840	-1.11590	1.05240
C	9.78070	-0.91250	-2.03540
C	9.61260	2.34120	-0.02000
C	9.86260	-1.04660	1.79360
H	9.79070	-0.94740	-3.12810
H	9.85090	-1.94450	-1.66830
C	10.96480	-0.08510	-1.51510
H	9.58470	2.53520	-1.09980
H	9.58720	3.30720	0.49170
C	10.89170	1.57610	0.34700
H	9.81040	-0.21650	2.50950
H	9.96430	-1.97260	2.36610
C	11.06460	-0.86190	0.85610
H	10.99320	0.86660	-2.05100
H	11.91350	-0.60450	-1.71780
N	10.77140	0.19620	-0.09970
H	11.00230	1.57410	1.43410
H	11.77390	2.08360	-0.07200
H	11.97730	-0.66520	1.43860
H	11.22630	-1.78880	0.30080

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Complex **3** with water molecules. SCF Energy: -2830.88398669.

Ir	-4.75120	-0.14390	0.23310
C	-6.88230	-0.13160	-0.28640
C	-6.64820	-1.02640	0.82320
C	-6.46440	1.19170	0.09960
C	-6.16730	-0.22140	1.93660
C	-6.03950	1.13100	1.49730
C	-6.61870	2.44010	-0.71220
H	-6.52620	2.23330	-1.77850
H	-7.60280	2.89070	-0.53920
H	-5.86360	3.18400	-0.45290
C	-5.69540	2.30870	2.35620
H	-5.25770	3.12230	1.77450
H	-6.59850	2.70520	2.83350
H	-4.99390	2.04060	3.14760
C	-5.88750	-0.74400	3.30890
H	-5.27960	-0.05010	3.88900
H	-6.83140	-0.90110	3.84310
H	-5.35280	-1.69290	3.26400
C	-6.99470	-2.48350	0.86800
H	-6.39190	-3.00270	1.61410
H	-8.05040	-2.61730	1.13250
H	-6.80970	-2.96150	-0.09560
C	-7.45690	-0.53300	-1.60620
H	-7.05880	-1.49820	-1.92310
H	-8.54580	-0.62050	-1.51680
H	-7.24030	0.20360	-2.38020
Cl	-3.05790	-1.61510	1.39580
C	-2.21540	0.37060	-1.20740
C	-2.47460	1.92520	0.51130
C	-0.87550	0.72960	-1.33190
C	-1.16390	2.34770	0.40930
H	-3.13970	2.34010	1.25540
C	-0.32430	1.68340	-0.48460
H	-0.25360	0.21990	-2.05520
H	-0.78220	3.12590	1.05700
N	-2.97900	0.93550	-0.24930
C	-2.89020	-0.68300	-2.08220
O	-4.14050	-1.02500	-1.54030
C	-3.11730	-0.06870	-3.48450
H	-2.17900	0.19680	-3.98070
H	-3.64240	-0.80150	-4.10170
H	-3.74090	0.82500	-3.40800
C	-2.02320	-1.95510	-2.19360
H	-2.58550	-2.70180	-2.75780
H	-1.07860	-1.77460	-2.71440

H	-1.81610	-2.36250	-1.20490
C	1.15920	1.95950	-0.47110
O	1.58910	3.09970	-0.59310
N	1.87850	0.82120	-0.28900
H	1.32500	-0.00310	-0.03840
C	3.27980	0.63820	-0.21850
C	3.72320	-0.68540	-0.08730
C	4.21650	1.67610	-0.27610
C	5.07930	-0.96570	-0.00230
H	2.99460	-1.48960	-0.06590
C	5.57290	1.37070	-0.19030
H	3.90700	2.70480	-0.37960
C	6.03960	0.05660	-0.04580
H	5.39930	-1.99780	0.08360
H	6.28250	2.18910	-0.24450
Si	7.85650	-0.32400	0.12730
O	8.19430	-0.22590	1.75870
O	8.00680	-1.87290	-0.47820
O	8.63200	0.85200	-0.76700
C	9.45030	0.11680	2.31580
C	9.00070	-2.80940	-0.10250
C	9.86880	0.69140	-1.43700
H	9.37480	0.02750	3.40300
H	9.68720	1.16280	2.08320
C	10.55390	-0.80620	1.77880
H	8.84880	-3.11540	0.94050
H	8.88380	-3.69750	-0.72980
C	10.40450	-2.21380	-0.27870
H	9.75540	-0.02720	-2.25880
H	10.14540	1.65450	-1.87480
C	10.95800	0.21500	-0.46420
H	10.40890	-1.80730	2.19220
H	11.54130	-0.45330	2.11360
N	10.45280	-0.89400	0.33000
H	10.60950	-2.10420	-1.34630
H	11.16200	-2.89920	0.13190
H	11.87380	-0.04360	-1.01720
H	11.20890	1.03390	0.21420
O	0.22840	-1.40110	0.75830
H	0.55190	-1.84020	1.55100
H	2.83160	4.59560	-0.53250
O	3.61170	5.13750	-0.71720
H	3.76700	4.96880	-1.65160
H	-0.74050	-1.40550	0.85900
H	-4.96230	-2.53040	-1.86440
O	-5.55410	-3.29290	-2.05940

H	-5.61030	-3.31340	-3.01870

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3-TiO_2. SCF Energy: -4559.34797067.

O	-3.58195	-1.91856	-3.36429
O	-3.49774	0.93272	3.64599
Ti	-3.42319	-1.49396	-1.59564
Ti	-0.29563	-0.95076	-1.88163
O	-1.48767	-2.29437	-1.19387
O	-4.93918	-0.48203	-1.88951
O	-3.79324	-3.09448	-0.84072
O	-1.96720	-0.09385	-2.16798
H	-2.12960	0.83081	-2.36684
O	-3.53984	-0.49291	0.14086
Ti	-3.38009	0.00098	2.08049
Ti	-0.25376	0.56357	1.84070
O	-1.44557	-0.86868	2.31134
O	-4.89707	0.94361	1.61562
O	-3.75113	-1.66884	2.66442
O	-1.92905	1.39050	1.48617
H	-2.09718	2.16668	0.94744
O	1.51283	-1.85905	-1.40693
O	0.11350	-1.84817	-3.43727
O	0.19775	1.00306	3.57301
O	5.20842	-1.78887	-1.48007
Ti	1.62120	-1.40859	0.45042
O	1.55494	-0.43345	2.09819
O	3.60719	-2.23496	0.76328
O	0.07304	-0.64873	0.16222
O	1.30158	-3.03504	1.11664
O	3.40380	0.11671	-0.20303
Ti	4.75656	-0.98868	0.24009
O	6.60774	-1.79957	0.55070
O	5.25044	-0.36321	2.02508
H	3.12943	0.99161	-0.60535
O	0.48146	0.77634	-1.93340
O	0.49177	1.84225	0.65712
Si	0.73406	2.06198	-0.95358
O	2.40783	2.35137	-1.13331
H	5.02534	-2.05206	-2.38480
H	5.08841	0.08134	2.86054
H	6.79069	-1.53626	1.45527
H	6.76968	-2.24421	-0.28488
H	3.31929	-3.08197	1.11163
H	0.66869	-3.70099	1.39511
H	-1.77552	-3.14146	-0.84583

H	-4.42613	-3.76044	-0.56225
H	-4.38403	-2.33481	2.94286
H	-5.12215	-0.74534	-2.79438
H	-3.41989	-2.36303	-4.19962
H	-0.06941	-2.11154	-4.34216
H	1.67496	-2.30358	-2.24226
H	1.73795	-0.17019	3.00308
H	0.03569	1.44752	4.40831
H	-3.31476	1.19603	4.55085
H	-5.05914	1.38808	2.45095
H	-4.37658	-0.05358	-0.02780
H	-1.73340	-1.71586	2.65923
H	2.72389	3.15089	-0.70111
C	-0.25822	3.53464	-1.52609
C	-0.57352	3.71054	-2.88391
C	-0.74215	4.48929	-0.61786
C	-1.33395	4.79442	-3.31084
H	-0.21937	2.98807	-3.61219
C	-1.50324	5.57374	-1.04846
H	-0.52039	4.37991	0.43921
C	-1.81495	5.74292	-2.40061
H	-1.56239	4.90612	-4.36651
H	-1.86447	6.29668	-0.32345
N	-2.56332	6.82049	-2.91983
C	-3.39996	7.66944	-2.25878
C	-4.09514	8.61619	-3.20443
O	-3.63028	7.68972	-1.05822
C	-3.37919	9.45792	-4.04539
C	-5.48738	8.60495	-3.29576
C	-4.03772	10.19113	-5.02963
H	-2.30089	9.50666	-3.97814
C	-6.08075	9.32949	-4.31050
H	-6.08462	7.99137	-2.63416
N	-5.37195	10.07346	-5.18013
C	-3.31798	11.11322	-6.01156
H	-7.14692	9.28314	-4.48140
Ir	-6.12260	10.74133	-7.06497
O	-4.21400	11.55259	-6.99915
C	-2.81471	12.35130	-5.23322
C	-2.13323	10.38840	-6.68675
Cl	-5.10944	8.54136	-7.79013
C	-8.32803	10.83384	-6.96819
C	-7.74542	12.15364	-6.73279
C	-7.94827	10.41364	-8.27846
C	-7.10682	11.44380	-8.86929
C	-7.03655	12.53715	-7.92654

H	-2.08046	12.09213	-4.46476
H	-2.34790	13.03951	-5.94168
H	-3.65524	12.86394	-4.76019
H	-1.67240	11.07531	-7.39948
H	-1.36931	10.07299	-5.97015
H	-2.50022	9.52402	-7.23781
C	-9.29138	10.13443	-6.05941
C	-8.01001	13.01926	-5.54034
C	-8.35936	9.14812	-8.95886
C	-6.55235	11.44119	-10.26100
C	-6.33465	13.83486	-8.16395
H	-9.11447	10.38339	-5.01120
H	-10.31816	10.43847	-6.29214
H	-9.23607	9.05021	-6.16656
H	-7.22486	13.76350	-5.40582
H	-8.96099	13.55134	-5.65856
H	-8.07129	12.43134	-4.62292
H	-8.66844	8.38729	-8.24244
H	-9.20109	9.34931	-9.63128
H	-7.53995	8.73313	-9.54494
H	-5.61224	11.99243	-10.31126
H	-6.35213	10.42274	-10.59553
H	-7.26664	11.89450	-10.95848
H	-5.41029	13.67721	-8.72122
H	-6.98266	14.49942	-8.74665
H	-6.09124	14.33522	-7.22639
H	-2.61308	6.85975	-3.94185
O	-2.88372	6.88307	-5.87487
H	-2.18652	6.93582	-6.53573
H	-3.23063	7.46967	0.87804
O	-2.65053	7.49038	1.65176
H	-2.06888	8.23189	1.45818
H	-3.66584	7.24580	-6.32726
H	-3.67459	12.12824	-8.55545
O	-3.46956	12.54595	-9.42343
H	-2.92830	13.30840	-9.20041

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